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# Calorimetric Debye temperature of Cu, Ag and Au

S. Tolpadi

*Department of Physics, Indian Institute of Technology, Kharagpur*

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The isochoric self-energy anharmonic effect which mainly depends on phonon-phonon interaction, has been considered to derive a modified specific heat equation. In the low temperature range, the Debye temperature obtained in the case of Cu, Ag and Au by considering the modified specific heat equation shows a shift towards the corresponding data calculated by using the modified theory of Paskin.

## 1. Introduction

Lowndes (1970) experimentally investigated the lattice anharmonicity on the long wavelength longitudinal optic modes of ionic crystals. He showed that in the low temperature region the phonon frequency shift due to isochoric self-energy effect in the case of KBr is much larger than the isothermal shift which is contrary to the perturbation calculations of Cowley (1963). The main difficulty of the perturbation method as pointed out by Cowley & Cowley (1965, 1966) is that the contributions from cubic anharmonicity and quartic anharmonicity are of opposite sign and therefore tend to cancel each other. Another difficulty of the method arises while choosing the third and fourth order derivatives of the potential function.

Recently (Tolpadi 1975) we introduced a thermodynamic method in which the isobaric and isochoric Grueneisen parameters were calculated from a knowledge of the temperature variation of the Debye frequency of an elastically isotropic solid. It was shown that the calculated data on frequency shifts, calorimetric and X-ray Debye temperature were in good agreement with experimental results. In a later work (1976a) we modified the Grueneisen relation of cubic crystals by considering the effect of isochoric Grueneisen parameter, its first order isochoric derivative and the first order isochoric derivative of the isothermal Grueneisen constant. In the present study we have evaluated the isochoric Grueneisen parameter of noble metals, its first order derivative and the effect of these anharmonic parameters on the specificheat, in the low temperature range. The Debye temperature calculated by using the modified specific heat equation shows a shift towards the value calculated by using a modified Paskin's theory (Tolpadi 1975, 1975a, 1976b).

## 2. Modified Heat Capacity Equation

The temperature variation of the phonon frequencies of a solid depends on isothermal and isochoric anharmonnic effects. The frequency shift $\Delta\nu$ of the

lattice dynamical energy levels within the limits of a quasi-harmonic model can be written as

$$\Delta\nu = \left(\frac{\partial\nu}{\partial T}\right)_v \Delta T + \left(\frac{\partial\nu}{\partial V}\right)_T \Delta V \qquad \ldots (1)$$

The term $\left(\frac{\partial\nu}{\partial T}\right)_v$ depends on phonon-phonon interactions (Maradudin & Fein 1962) and is called the self-energy shift whereas the term $\left(\frac{\partial\nu}{\partial V}\right)_T$ gives the frequency shift due to the change in the interatomic force constant. We now define the isothermal and isochoric Grueisen parameters and their first order derivatives which are given by

$$\left.\begin{aligned} \gamma_T &= -\frac{V}{\nu}\left(\frac{\partial\nu}{\partial V}\right)_T, \quad \mu_v = \frac{T}{\gamma_T}\left(\frac{\partial\gamma_T}{\partial T}\right)_v, \mu_T = \frac{V}{\gamma_T}\left(\frac{\partial\gamma_T}{\partial V}\right)_T \\ \gamma_v &= -\frac{T}{\nu}\left(\frac{\partial\nu}{\partial T}\right)_v, \quad \sigma_v = \frac{T}{\gamma_v}\left(\frac{\partial\gamma_v}{\partial T}\right)_v, \quad \sigma_T = \frac{V}{\gamma_v}\left(\frac{\partial\gamma_v}{\partial V}\right)_T \end{aligned}\right\} \ldots (2)$$

Introducing the values of $\gamma_T$ and $\gamma_v$ in eq. (1) we can show that

$$\Delta\nu = \nu(\gamma_v\Delta T/T + \gamma_T\Delta V/V \qquad \ldots (3)$$

$$\gamma_p = -\frac{V}{\nu}\left(\frac{\partial\nu}{\partial V}\right)_p \quad \gamma_T + \gamma_v/\alpha T \qquad \ldots (4)$$

where $\alpha$ is the thermal expansion coefficient and $\gamma_p$ is the isobaric Grueisen parameters.

Earlier workers (Grueisen 1926, Slater 1939) assumed that the isothermal Grueisen parameter $\gamma_T$ is the same for all the $3N$ phonon frequencies. Recently (Tolpadi 1975b) we observed that the isobaric Grueisen parameter $\gamma_p$ does not vary significantly within the Brillouin zone. We can therefore assume that the isochoric Grueisen parameter $\gamma_v$ given in eq. (3) at a given temperature of the crystal is independent of the phonon frequencies. Further the quantity $\Delta\nu/\nu$ given in eq. (3) is a constant when the temperature and volume of the crystal change under constant atmospheric pressure. It may be noted that the lattice dynamical energy levels of the $3N$ modes of vibration are changed by a constant factor $(1 + \Delta\nu/\nu)$. The Helmholtz free energy $F$ of the crystal can now be obtained by substituting the anharmonic frequencies in the harmonic formula. While discussing the heat capacity equation, Wallace (1972) has shown that the heat capacity is correctly given in the low temperature range if the renormalised frequencies are considered in the harmonic formula. We can therefore show that

the Helmholtz free energy and the internal energy $U$ of the crystal are given by

$$F(V, T) = \phi + \sum_{i}^{3N} \{h\nu_i/2 + kT \ln (1-\exp(-h\nu_i/kT))\} \quad \ldots (5)$$

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_v = \phi + (1 + \gamma_v)E \quad \ldots (6)$$

where $\phi$ is the static lattice potential and $E$ is the sum of the zero point and thermal energy of the crystal.

Differentiating the internal energy $U$ given in eq. (6) with respect to temperature at constant volume and using the result

$$(\partial E/\partial T)_v = C(1 + \gamma_v) \quad E\gamma_v/T, \text{ we get}$$

$$C_v = (1 + \gamma_v)\{(1 + \gamma_v)C - E\gamma_v/T\} + E\sigma_1\gamma_v/T \quad \ldots (7)$$

where $C_v$ is the observed specific heat.

$C$ appearing in eq (7) is the specific heat function which is defined as

$$C = k \sum_{i=1}^{3N} \frac{(h\nu_i/kT)^2 \exp (h\nu_i/kT)}{(\exp (h\nu_i/kT) - 1)^2} \quad \ldots (8)$$

It is found that $\gamma_v$ is much less than 1 and therefore the modifieds pecific heat equation which follows from eq. (7) can be written as

$$C = C_v - G \quad \ldots (9)$$

where

$$G = \gamma_v C_v\{2 + (\sigma_v - 1)E/TC_v\} \quad \ldots (10)$$

The quantity $G$ is the isochoric self-energy correction, to the observed specific heat $C_v$ of the crystal, which depends on phonon-phonon interactions (Maradudin & Fein 1962).

## 3. Evaluation of Isobaric Gruneisen Parameter

An average isobaric Gruneisen parameter $\gamma_p$ has been calculated in the low temperature range adopting the following procedure. In this temperature range a major contribution to the specific heat of the crystal is by the long wavelength acoustic modes. Differentiating the frequency expressions obtained from the frequency determinant in the $\lambda \to \infty$ limit, the nine expressions for the isobaric phonon Gruneisen parameters along the three symmetry directions are given by

(100) direction

$$\gamma_1 = \gamma_2 = -\frac{1}{2\alpha Q_1}\left(\frac{\partial Q_1}{\partial T}\right)_p = \frac{1}{6} \qquad (T_1, T_2)$$

$$\gamma_3 = -\frac{1}{2\alpha Q_2}\left(\frac{\partial Q_2}{\partial T}\right)_p = \frac{1}{6} \qquad (L)$$

(110) direction

$$\gamma_4 = \gamma_1 \qquad (T_1)$$

$$\gamma_5 = -\frac{1}{2\alpha Q_3}\left(\frac{\partial Q_3}{\partial T}\right)_p = \frac{1}{6} \qquad (T_2) \qquad \ldots \quad (11)$$

$$\gamma_6 = -\frac{1}{2\alpha Q_4}\left(\frac{\partial Q_4}{\partial T}\right)_p = \frac{1}{6} \qquad (L)$$

(111) direction

$$\gamma_7 = \gamma_8 = -\frac{1}{2\alpha Q_5}\left(\frac{\partial Q_5}{\partial T}\right)_p = \frac{1}{6} \qquad (T_1, T_2)$$

$$\gamma_9 = \frac{1}{2\alpha Q_6}\left(\frac{\partial Q_6}{\partial T}\right)_p = \frac{1}{6} \qquad (L)$$

where $Q_1 = c_{44}$, $Q_2 = c_{11}$, $Q_3 = (c_{11} - c_{12})$, $Q_4 = (c_{11} + c_{12} + 2c_{44})$ $Q_5 = (c_{11} - c_{12} + c_{44})$, $Q_6 = (c_{11} + 2c_{12} + 4c_{44})$ and $c_{ij}$ are the elastic constants. In eq. (11) $T_1$, $T_2$ and $L$ refer to transverse and longitudinal polarisations.

An average isobaric Grueisen parameter is obtained by using a 3-term Houston's formula (Betts *et al* 1956) which is given by

$$\bar{\gamma}_p = (10\,\bar{\gamma}_A + 16\bar{\gamma}_B + 9\bar{\gamma}_C)/35 \qquad \ldots \quad (12)$$

where $\bar{\gamma}_A = \bar{\gamma}_B$ and $\bar{\gamma}_C$ are the average isobaric Grueisen parameters along the (100), (110) and (111) directions.

## 4. Determination of the Parameters $\sigma_T$, $\sigma_v$, $\mu_T$ and $\mu_v$

The expression for the parameter $\sigma_v$ appearing in eq. (10) is obtained as follows. Treating $\Delta\nu$ given in eq. (3) as an exact differential we can show that (Tolpadi 1976, 1976a)

$$\sigma_T = \mu_v \gamma_T / \gamma_v \qquad \ldots \quad (13)$$

If the temperature and volume of the crystal are changed under constant atmospheric pressure we can write

$$d\gamma_v = \left(\frac{\partial \gamma}{\partial T}\right)_v dT + \left(\frac{\partial \gamma_v}{\partial V}\right)_T dV \qquad \ldots \quad (14)$$

$$= \gamma_v(\sigma_v dT/T + \sigma_T dV/V)$$

Rearranging eq. (14) we get

$$\sigma_v = T\left\{\frac{1}{\gamma_v}\left(\frac{\partial \gamma_v}{\partial T}\right)_P - \alpha\sigma_T\right\} \qquad \ldots \quad (15)$$

The expressions for $\gamma_T$, $\mu_T$ and $\mu_v$ are taken from an earlier work (Tolpadi 1974) and they are given by

$$\gamma_T = \frac{V}{E}\frac{d\phi}{dV}$$

$$\mu_T = 1+\gamma_T\left(1-\frac{TC}{E}\right)+\frac{V}{\gamma_T E}\left(B_T - V\frac{d^2\phi}{dV^2}\right) \quad \ldots (16)$$

$$\mu_v = T\left\{\frac{1}{\gamma_T}\left(\frac{\partial\gamma_T}{\partial T}\right)_p - \alpha\mu_T\right\}$$

where $B_T$ is the bulk modulus of the crystal.

The energy $E$ appearing in eqs (16) and (10) is calculated by using a Debye model of the solid. We have

$$E = E(T)+9R\theta/8 \quad \ldots (17)$$

where $E(T)$ is the thermal energy and $9R\theta/8$ is the zero-point energy (Seitz 1940).

## 5. Results and Discussion

In the present work, the temperature variation of the calorimetric Debye temperature $\theta$ of Cu, Ag and Au has been investigated in the low temperature region. The parameters $\bar{\gamma}_p$, $\gamma_T$, $\mu_T$, $\mu_v$, $\gamma_v$, $\sigma_v$ and $\sigma_T$ have been calculated by using eqs. (12), (16), (4), (13) and (15) respectively. The energy $E$ has been obtained by assuming an appropriate Debye temperature. The experimental results on the bulk modulus, the thermal expansion coefficient and the elastic constant data are taken from relevant source (Gray 1972, Simmons & Wang 1971). The calculated data on the anharmonic parameters is given in table 1

Table 1. Temperature variation of the anharmonic parameters of Cu, Ag and Au

| Crystal | Temperature (K) | Anharmonic parameters | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\bar{\gamma}_p$ | $\gamma_T$ | $\mu_T$ | $\mu_v \times 10^2$ | $\gamma_v \times 10^3$ | $\sigma_T \times 10^{-1}$ | $\sigma_v$ |
| Cu | 40 | 2.2 | 1.06 | 4.9 | 7.8 | 0.31 | 27 | 5.7 |
| | 60 | 3.0 | 1.10 | 4.8 | 11 | 1.9 | 6 4 | 2.8 |
| | 90 | 3.1 | 1.18 | 4.6 | 15 | 4.9 | 3.6 | 1.6 |
| | 120 | 3.1 | 1.26 | 4.4 | 24 | 8.2 | 3.7 | 2.2 |
| | 160 | 3.4 | 1.38 | 4.1 | 29 | 17 | 2.3 | 1.7 |
| Ag | 38 | 8.2 | 1.20 | 8.8 | 15 | 4.6 | 3.9 | 0.14 |
| | 50 | 5.3 | 1.27 | 8.6 | 19 | 5.1 | 4.7 | 0.73 |
| | 75 | 4.4 | 1.38 | 8.1 | 25 | 8.4 | 4.1 | 0 43 |
| | 100 | 3.7 | 1.51 | 7.5 | 30 | 9.6 | 4.7 | 0.06 |
| | 125 | 3.3 | 1.63 | 6.8 | 34 | 9.8 | 5.6 | 0.14 |
| Au | 30 | 9.3 | 1.32 | 7.2 | 5.4 | 3.4 | | |
| | 50 | 8.7 | 1.35 | 7.1 | 25 | 8.5 | 4.0 | 0.05 |
| | 75 | 4.2 | 1.66 | 7.0 | 53 | 5.8 | 15 | −1.0 |
| | 125 | 2.9 | 2.06 | 6.5 | 30 | 4.1 | 15 | −1.4 |

Assuming a Debye model of the crystal, the Debye temperature is estimated by considering that the observed specific heat refers to a Debye specific heat function. It is found that $\theta$ decreases and then increases with temperature in the case of copper and silver. But in the case of gold $\theta$ increases with temperature. These results are given in figure 1 The relevant $\theta$ values in the case of Cu, Ag and Au when T °K may be assumed to be 343K, 225K and 162K respectively (Wallace 1972). In figure 1 we have also plotted the values obtained by using the modified theory of Paskin (Tolpadi 1975, 1975a, 1976b) which includes the crystal anharmonicity due to both volume expansion and isochoric self-energy effect.

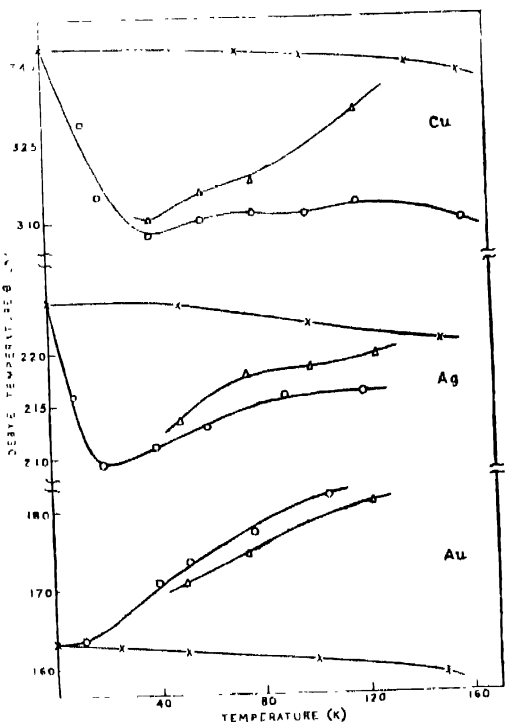


Fig 1. Calorimetric Debye temperature of copper, silver and gold. $X-X-X$ modified theory of Paskin; $\Delta-\Delta-\Delta$ calorimetric Debye temperature after applying anharmonic correction; $0-0-0$ calorimetric Debye temperature without applying correction

In the case of copper and silver $\theta$ value calculated by using the modified theory of Paskin is more than the corresponding calorimetric data. But in the case of gold the calorimetric data is more than the $\theta$ values obtained from the modified theory of Paskin.

Using the data given in table 1 the isochoric anharmonic correction $G$, to the observed specific heat $C_v$, is calculated from eq. (10). The Debye temperature of

the crystal is now calculated from eq. (9) by assuming that $C$ refers to a Debye specific heat function. The calculated data on $\theta$ values is given in figure (1). It may be noted that $G$ is $+ve$ in the case of Cu and Ag and therefore the $\theta$ values calculated by applying the correction $G$, shows a shift towards the data based on the modified theory of Paskin. But in the case of Au $G$ is $-ve$ in the temperature range 60 to 140K and it is interesting to note that the $\theta$ values calculated by applying the isochoric correction also shows a shift towards the results based on the modified theory of Paskin.

The trend of our calculation shows that the anharmonic correction $G$ may be neglected when the temperature of the crystal $T \leq \theta/10$. In this low temperature region, contribution to $C_v$ is mainly from lattice vibrations and free electrons in metals. In our present work therefore values of Debye temperature $\theta_0$ obtained from the plot of $C_v/T$ against $T^2$ has been assumed to be 342, 225 and 162K respectively in the case of Cu, Ag and Au (Wallace 1972). It may further be noted that if the effect of electrinic specific heat is included in our calculation $\theta$ calculated from the modified specific heat equation tends to increase slightly as compared to the data plotted in figure 1. The Debye temperature calculated in the low temperature region in the case of Cu, Ag and Au by applying the isochoric self-energy correction shows a shift towards the elastic data which is obtained by using a modified theory of Paskin. This shift indicates that the isochoric self-energy correction to the observed specific heat which depends on phonon-phonon interactions, must be applied so that the values calculated by using two independent methods based on elastic and calorimetric data may show better agreement. This is not surprising because the modified theory of Paskin refers to acoustic phonons with $\lambda \to \infty$. The major contribution to the specific heat in the low temperature region is also from acoustic modes and therefore $\theta$ calculated by applying the self-energy correction to the observed specific heat shows the expected shhift towards the data which is based on modifiedtheory of Paskin.

The main assumption introduced in the present investigation is that the isothermal Gruneisen parameter and two of its first order derivatives are the same for all the phonon frequencies. In view of the difficulties in the perturbation method, a simple thermodynamic theory is introduced to calculate an average isochoric Gruneisen parameter and its first order derivatives. The thermodynamic theory introduced in the present work suggests a simple method of including the effect of isochoric anharmonicity on internal energy, entropy and specific heat of crystalline solids.

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